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Relative Signs of the $^{31}P-^{1}H$ and $^{31}P-C-^{1}H$ n. m. r Coupling Constants

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Relative Signs of the $^{31}P-^{1}H$ and $^{31}P-C-^{1}H$ n. m. r. Coupling Constants.[1]

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Sir:

The possibility that terms other than Fermi contact interaction make significant contributions to nuclear spin-spin coupling with heavy nuclei has stimulated considerable interest in the n. m. r. spectra of compounds containing heteroatoms. In particular, relative signs and magnitudes of J_{XCH} and J_{XCCH} have been reported for ethyl derivatives of several heavy isotopes of spin 1/2.[2] In order to understand better

(2) For a summary and references, see G. Klose, Ann. Physik, 9, 262 (1962); P. T. Narasimhan and M. T. Rogers, J. Chem. Phys., 34, 1049 (1961).

the factors responsible for spin coupling with a representative heavy nucleus, we have analyzed the spectra of $(CH_3)_3P$, $(CH_3)_2PH$ and $(CH_3)PH_2$ and have obtained relative signs and magnitudes of J_{PH} and J_{PCH}.

The proton spectrum of methylphosphine (Fig. 1) may be treated as the superposition of an A_3B_2 and an A_3X_2 spectrum, using the method of effective chemical shifts.[2] Inspection of the spectrum suggests that the methyl region can be separated into a triplet at lower field and a more complicated group of lines at higher field.

Association of the triplet with the simpler half of the P–H spectrum, also occurring as the lower field part, immediately suggests that J_{PH} and J_{PCH} have the same sign. The spectrum observed for CH_3PH_2 and the spectrum calculated using the parameters in the table are shown in Fig. 1. In both methyl– and dimethylphosphine J_{PH} and J_{PCH} have the same sign; double-resonance experiments performed by Drs. G. Juvinall and S. L. Manatt of the Jet Propulsion Laboratory confirm this conclusion.

TABLE I[a]

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR PHOSPHINE DERIVATIVES

Compound	J_{PH}	J_{PCH}	J_{HCPH}	ν_H	ν_{CH_3}
PH_3[b]	182.2				
CH_3PH_2	±186.4	±4.1	8.2	157.7	58.5
$(CH_3)_2PH$	±191.6	±3.6	7.7	187.7	63.8
$(CH_3)_3P$		2.7			56.3

[a]Chemical shifts and coupling constants were moderately temperature dependent; the values reported are for 33°. Chemical shifts are given in cps at 60 Mcps from TMS as internal standard.

[b]R. M. Lynden-Bell, Trans. Faraday Soc., 57, 888 (1961).

Anet[3] has recently demonstrated by double-resonance experiments that $J_{^{13}CH}$ and J_{HCH} have opposite sign in $H_2D^{13}COH$; Lynden-Bell and Sheppard[4] have reached the same conclusion for $J_{^{13}CH}$ and $J_{^{13}CCH}$

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(3) F. A. L. Anet, J. Am. Chem. Soc., 84, 3767 (1962).

[4] R. M. Lynden-Bell and N. Sheppard, Proc. Roy. Soc., A269, 385 (1962).

in $H_3{}^{13}C{}^{13}CH_3$ by analysis of the high resolution spectrum.[4] In contrast, J_{PH} and J_{PCH} have the same sign. Theoretical treatments have indicated that contact interaction will dominate the coupling of directly bonded atoms[5]; more approximate treatments of HCH[6] and ^{13}CCH [7] lead to the same conclusion.

(5) M. Karplus and D. M. Grant, Proc. Natl. Acad. Sci., 45, 1269 (1959); N. Muller and D. E. Pritchard, J. Chem. Phys., 31, 768, 1471 (1959); J. N. Shoolery, ibid., 31, 1421 (1959).

(6) H. S. Gutowsky, M. Karplus and D. M. Grant, J. Chem. Phys., 31, 1278 (1959) and references therein.

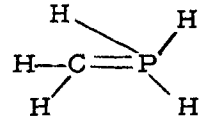
(7) G. T. Karabatsos, J. D. Graham and F. Vane, J. Phys. Chem., 65, 1657 (1961).

The observed difference in relative sign of J_{XH} and J_{XCH} for X = ^1H, ^{13}C and for X = ^{31}P suggests that some mechanism other than the usual σ-bond interactions contribute to spin-spin coupling with phosphorus. Spin-orbital and electron-dipole interaction would be expected to be relatively more important in coupling to ^{31}P than to ^1H or ^{13}C due both to the greater anisotropy of the screening around phosphorus[8] and to the relatively small degree of s character of its bonding orbitals.[9] However, Klose has been able to justify the spectrum of

(8) J. A. Pople, Mol. Phys., 1, 216 (1958).

(9) The bond angles in methylphosphine suggest that the phosphorus bonding orbitals in this compound have predominantly p-character: $\angle CPH = 97°30'$, $\angle HPH = 93°23'$. See E. L. Breig and C. C. Liu, J. Chem. Phys., 35, 2139 (1961).

$(CH_3CH_2)_3P$ semiquantitatively by a valence-bond treatment using only contact interactions.[2] Alternately, the d orbitals and non-bonding electrons of phosphorus may be involved in coupling through structures of the "ylene" type (I).[10] Spin-orbital or magnetic-dipole



I

(10) This structure is analogous to the hyperconjugative structures used to explain long-range coupling in hydrocarbons. Although unimportant in determining the total energy of the molecule, such structures may be very important in spin-spin coupling. See R. A. Hoffman and S. Gronowitz, Arkiv. Kemi., 16, 471 (1960).

interactions might give J_{PCH} the observed sign; important contributions from I certainly would. It is not possible to decide which factor is most important on the basis of available experimental evidence.

It is unfortunately not possible to assign an absolute sign to J_{PH}, although such an assignment would be of considerable interest. Recent calculations for several paramagnetic transition metal ions indicate that the contributions of a spin-polarized 3s orbital to the contact term may be opposite in sign to that of a 1s or 2s orbital[11]; this result

(11) V. Heine, Phys. Review, 107, 1002 (1957); R. E. Watson and A. J. Freeman, ibid., 120, 1125, 1134 (1960).

suggests that J_{PH} may be either positive or negative, depending upon the relative contributions of the 1s, 2s and 3s electrons to the coupling.

Acknowledgement. - We are deeply indebted to Dr. F. C. Caserio, Jr., for the phosphine samples used in this research.

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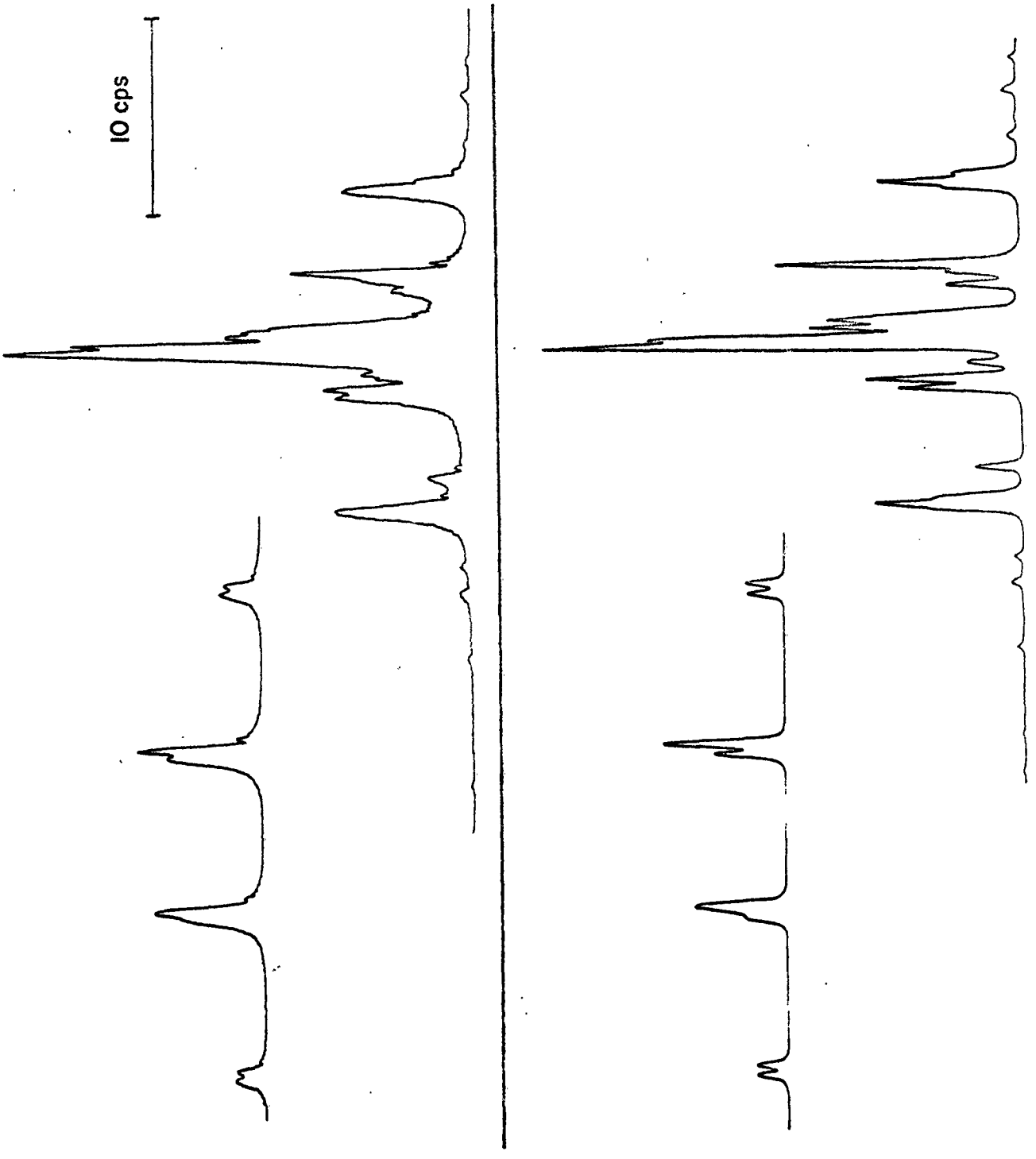
Fig. 1. Observed (upper) and calculated (lower) proton n. m. r. spectra of methyl phosphine at 60 Mcps. The spectral parameters used in the calculated spectrum are given in Table I.



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